Visible-Light Upconversion Carbon Quantum Dots Decorated TiO₂ for the Photodegradation of Flowing Gaseous Acetaldehyde

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A B S T R A C T

Carbon-modified photocatalyst has attracted extensive attentions in the field of gaseous pollutant removal, mainly due to the improved adsorption properties and electronic transport of carbon matrix, such as carbon nanotubes, graphene, and fullerene, etc. In this work, carbon quantum dots (CQDs) were employed to enhance the photocatalytic performance of TiO₂-based composites for flowing gaseous acetaldehyde removal. Besides the aforementioned advantages of carbon materials, the unique up-converted photoluminescence property of CQDs is capable of extending the optical absorption to visible-light range. Moreover, the electron spin resonance (ESR) results firstly verified a stable existence of Ti³⁺ defect in the CQDs/TiO₂ composite, which is possibly induced by the electron migration from CQDs to TiO₂. And the formed Ti³⁺ donor energy level in the band gap could further help with the visible-light harvesting. During the photodegradation experiments, with two-hour continuous flowing gaseous acetaldehyde injection (500 ppm, 20 sccm), the CQDs/TiO₂ composite remained 99% removal efficiency under fluorescent lamp irradiation (λ > 380 nm). The optimized CQDs content was obtained as 3 wt%, and the underlying mechanism was further analyzed by temperature programmed desorption (TPD) methods. This work will push forward the air purification researches by providing new insights of CQDs sensitized photocatalyst.

1. Introduction

Volatile organic compounds (VOCs) are the dominating indoor contaminants that can be released from cooking fuels, house furnishings, or any chemical involved material [1]. As it is reported that time-weighted exposure to indoor pollutants may cause high rates of morbidity and mortality, the indoor air quality is rather important to human's health [2–4]. A notorious example is acetaldehyde, which is usually accompanied with the oxidation of unsaturated fatty acids or the cleavage of photo initiators under light, or even the hydrolysis of some composite building materials containing esters [5]. With a highly reactive nature, acetaldehyde not only directly threatens human's health due to its cytotoxicity, mutagenicity, and carcinogenicity, but also readily participates in rearrangement of chemical compounds through further reacting with O₃, NOx and other reactive gases [5,6].

In the latest, photocatalytic oxidation (PCO) technology has been progressively applied in indoor air purification, due to its room-temperature feasibility, environmental friendliness and chemical activity toward most of contaminants [7–9]. Through the PCO process, most organic molecules could be photodegraded into smaller benign products such as CO₂ and H₂O. Various photocatalysts have been investigated and applied into PCO field, among which TiO₂ photocatalyst has been most widely studied, owing to its comprehensive properties of good chemical stability, superior photocatalytic oxidation ability and outstanding biocompatibility [10]. However, with relatively broad band gap (~3.2 eV), TiO₂ photocatalyst can only be activated by ultraviolet light. Besides, the high electron-hole recombination efficiency of TiO₂ also confines the photocatalytic behavior. Many efforts hitherto have been made to ameliorate the photocatalytic ability, including metal [11] or non-metal [12] ion doping, dye-sensitization [13,14], heterojunction with narrow-bandgap semiconductors [15,16] or noble metals [17–19].

Recently, carbon quantum dots (CQDs) has been identified to sensitize some semiconductors, such as TiO₂ [20], g-C₃N₄ [21], Bi₂S₃ [22], CdS [23], for enhancing optical responsiveness and photocatalytic performance. Compared with graphene [24], carbon nanotube [25] and fullerene [26,27], the zero-dimensional CQDs
products were named as [29]. Up to now, most the reports of CQDs-based TiO2 composites to high-energy light via the multiple photon-absorption of CQDs (UCPL) property, capable of transferring low-energy light to high-energy light via the multiple photon-absorption of CQDs [29]. Up to now, most the reports of CQDs-based TiO2 composites concentrate on the study of water-based photocatalytic process, such as photo-degradation of organic dyes (e.g. methyl blue and RhB), and photocatalytic water splitting [29–32]. However, the photocatalytic effect of CQDs/TiO2 composites involved the oxidation of gaseous pollutants has been rarely investigated, particularly for these flowing gaseous organic compounds. Both of CQDs and TiO2 are easily attainable and nontoxic, and thus it is of theoretical and practicable favor to construct CQDs/TiO2 composite photocatalyst for enhancing the visible-light-driven photocatalytic ability and apply it into the indoor air purification.

Herein, we synthesized CQDs/TiO2 composites through a facile method. The photocatalytic performance and mechanism of decomposing flowing gaseous acetaldehyde were investigated. After decorating with CQDs, the modified TiO2 photocatalyst shows an enhanced photodegradation ability under visible light irradiation and suggests a good application in indoor air purification. Additionally, a favorable defect of Ti2+ has been unexpectedly detected in the TiO2 matrix after CQDs modification, which not only demonstrates an interfaced electron migration and also further enhances the visible-light photocatalysis.

2. Experimental section

2.1. Synthesis of CQDs/TiO2 photocatalysts

All reagents, including commercial TiO2 powder (P25), urea and citric acid (AR, Sinopharm Chemical Reagent Corp, China) were used as received without any further purification.

CQDs synthesis involves a hydrothermal method based on a previous report [33]. Briefly, 1.0 g urea and 1.0 g citric acid were dissolved in 15 ml ultrapure water and then the mixture was transferred into 30 ml Teflon autoclave at 180 °C for 6 h. After cooling down to room temperature, the product (dark green solution), was centrifugated at 12,000 rpm for 20 min to remove the large particles. The remaining solvent was dried at 80 °C for 10 h to obtain black CQDs solid.

CQDs/TiO2 composite photocatalysts were prepared according to previous report [29]. P25 was ultrasonically dispersed into 20 ml ethanol, and the CQDs was dissolved into 15 ml ultrapure water. Then, the CQDs solution was dropwise added into the stirring P25 suspension, and the mixture stirred to be dried. The obtained solid mixture was calcined at 300 °C for 3 h in the muffle furnace. Then, the substance was washed with ultrapure water and ethanol for several times, and dried for 24 h at room temperature to obtain the CQDs/TiO2 composites. The collected CQDs/TiO2 products were named as x wt% CQDs/TiO2, where x = 1, 3, 7, represent the mass percentage of CQDs to TiO2 in the composites.

2.2. Characterizations

The morphology and crystallography of the samples were investigated by high-resolution transmission electron microscopy (HTEM, JEM-2100F). The crystal structures of the samples were characterized by X-ray diffractometer (XRD, Rigaku D/Max 2200PC) with Cu Kα radiation. Fourier transform infrared (FTIR) spectra were measured by a Thermal Scientific 5225 Verona Rd with the KBr pellet technique. X-ray photoelectron spectroscopy (XPS) data were recorded by a Thermal Scientific ESCALAB-250 using Al Kα radiation line source and the binding energies were calibrated by setting O 1s peak of pristine TiO2 to 530.26 eV. Diffuse reflectance ultraviolet–visible (UV–Vis) spectra were obtained on a Shimadzu UV-3600 spectrometer by using BaSO4 as reference. Photoluminescence (PL) spectra of the samples were examined at room temperature by an Edinburgh Instruments FLSP-920 fluorescence spectrophotometer with an excitation wavelength of 320 nm.

Electron spin resonance (ESR) signals of reactive species spin-trapped by 5,5-dimethyl-L-pyrroline-N-oxide (DMPO) were determined on a JES-FA200 spectrometer. Photocatalysts were dispersed in DMPO/ethanol solution and DMPO/H2O solution for detection of superoxide radicals (·O2-) and hydroxyl radicals (·OH), respectively. A 500 W xenon lamp was used as the irradiation source.

2.3. Photocatalytic activity measurements

The photocatalytic performance of CQDs/TiO2 composites for flowing gaseous acetaldehyde degradation was conducted in a reactor chamber which was a 300 cm3 cuboid quartz vessel (20 cm × 10 cm × 1.5 cm) with an inlet and an outlet for gas flow. This chamber is connected to an online photocatalysis test system combining with gas chromatograph (SP 502, high purity nitrogen as carrier gas), to detect the flowing acetaldehyde concentration. All the photocatalytic experiments were carried out at room temperature, using a fan cooling system to maintain the thermal condition, and the relative humidity was kept at ~45%.

The photocatalytic experimental samples were prepared through a coating method. In brief, 0.1 g photocatalyst was ultrasonically dispersed in ethanol, and the slurry was homogeneously coated onto a glass plate to form a thin film (6 cm × 13 cm). After being dried, the tested sample was transferred into the reactor chamber, and gaseous acetaldehyde (500 ppm) mixed with air flowed into the chamber at 20 sccm flow rate. The photocatalytic experiments contained the following steps: first, the photocatalyst fully adsorbed acetaldehyde to reach an adsorption/desorption equilibrium in the dark condition (the GC detection showed a reenhanced concentration of acetaldehyde); second, with light irradiation, the gaseous acetaldehyde continuously flowed through the reactor chamber and the concentration was measured by GC with 5 min intervals. Household fluorescent lamps (4 × 65 W, λ > 380 nm) and a xenon lamp with UV-cut filter (λ > 400 nm) were used as the irradiation sources in the photocatalytic process. The efficiency for photo-decomposing acetaldehyde was calculated as follows:

\[ \eta = \frac{C_0 - C}{C_0} \times 100\% \]

where \( C_0 \) presents the original acetaldehyde concentration after it reaching an adsorption/desorption equilibrium on photocatalysts, and C is the real-time acetaldehyde concentration detected during the photodegradation process.

2.4. Photoelectrochemical measurements

The photoelectrochemical measurements of CQDs/TiO2 were performed on a CHI 660A electrochemical workstation (Chenhua Instrument, Inc.). Three-electrode system consisting of platinum wire as counter electrode, Ag/AgCl in saturated KCl as reference electrode and sample-coated fluorine-doped tin oxide substrate (FTO) as working electrode was used for the measurement. 1 M NaCl solution was used as electrolyte. The working electrode was prepared as follows: 100 mg sample was ultrasonically dispersed into 2.0 g ethanol for 1 h, then 300 μL slurry was spin-coated at 1000 rpm for 20 s to form a 1 cm × 2.5 cm sample film onto the FTO substrate. Finally, the FTO substrate with sample film was
dried at 80 °C for 30 min. A xenon lamp with UV-cut filter (λ > 400 nm) was used as the irradiation source in the photocurrent test.

2.5. Acetaldehyde-TPD measurements

The acetaldehyde temperature-programmed desorption (acetaldehyde-TPD) measurements were carried out by PCA-1200 equipped with a thermal conductivity detector. For acetaldehyde-TPD, 400 mg sample was soaked in N2 flow at 120 °C for 1 h first, and then cooled to 30 °C and adsorbed flowing gaseous acetaldehyde for 2 h. After purging with N2 for 10 min to remove the unadsorbed acetaldehyde in the pipeline, the sample in N2 flow was heated at the rate of 10 °C min⁻¹ to obtain the acetaldehyde-TPD profile.

3. Results and discussion

3.1. Characterizations of CQDs/TiO2

In this experiment, CQDs with averaged size of 4–5 nm has been successfully synthesized, which owned a well-crystallized core and an amorphous shell as revealed in the HRTEM image (Fig. S1). Notably, in the up-converted photoluminescence spectra (Fig. S2), with the excitation wavelength ranging from 600 nm to 800 nm, the CQDs can irradiate up-converted emissions located in the range of 375–550 nm, which suggests that the synthesized CQDs could desirably convert those visible or near-infrared light to short-wavelength light with higher photon energy.

According to the overall TEM image of CQDs/TiO2 composites in Fig. 1a, it reveals a coupling structure that several monodispersed CQDs (4–5 nm in diameter) attach to the surface of TiO2 particles, which are 20–30 nm in diameter. As shown in Fig. 1b, the interplanar spacing of 0.249 nm and 0.187 nm belong to the (1 0 1) plane of rutile TiO2 and the (2 0 0) plane of anatase TiO2, respectively (JCPDS card no. 21-1276 and no. 21-1272), while the interplanar spacing of 0.217 nm is assigned to the (0 0 1) plane of graphene carbon. And that demonstrates the successful coupling of CQDs with TiO2. To further confirm the CQDs are well decorated on TiO2, the FTIR spectra (Fig. 1c) of CQDs/TiO2 were carried out. Compared with the pristine TiO2, some new functional groups can be observed in CQDs-modified TiO2. The typical absorption peaks at 1635 cm⁻¹ and 3420 cm⁻¹ are assigned to the vibration of water absorbed on the surface of substance. The new appeared peaks in CQDs/TiO2 composite at 2974 cm⁻¹ (CH2), 1226 cm⁻¹ (CH), 1157 cm⁻¹ (C=O) are ascribed to the addition of CQDs [29], evidently confirming the existence of CQDs in the CQDs/TiO2 composites. Although the XRD patterns only show the characteristic diffraction line of anatase and rutile phases belonging to TiO2 (Fig. 1d), the existence of CQDs cannot be ignored, which is resulted from very slight amount of CQDs in the composites.

Subsequently, XPS was employed to further investigate the interaction between CQDs and TiO2. The full survey spectrum of the CQDs/TiO2 composite, indicating the presence of titanium (Ti 2p), carbon (C 1s) and oxygen (O 1s), is showed in Fig. 2a. In Fig. 2b, two fitted peaks of 3 wt% CQDs/TiO2 composite located at 459.3 and 464.91 eV could match with the Ti 2p3/2 and Ti 2p1/2 of TiO2 [34,35], the subdued binding energy compared with pristine TiO2 implying that the chemical environment of Ti has changed after combining with CQDs. In the C 1s spectrum (Fig. 2c), the dominated peak referring to C–C bond with sp² orbital mainly belongs to surface carbon contaminate [36], and the peak shifts from 287.14 eV to 285.65 eV after cooperating with CQDs. Due to the different carbon's chemical valence state between electroneutral CQDs and surface carbon contaminate with positive charged

![Fig. 1. Morphological and structure characterizations of CQDs/TiO2 composites. (a) Overall TEM image of 3 wt% CQDs/TiO2 sample. (b) Zoom-in HRTEM image of the marked region in (a). (c) FTIR spectra of pristine TiO2, 3 wt% CQDs/TiO2 and CQDs sample. (d) XRD patterns of CQDs/TiO2 composites with different CQDs content.](image-url)
carbon, it is reasonable after adding CQDs the binding energy of C–C bond reduced. Additionally, No peak corresponding to Ti–C bond at around 281 eV was observed [37], suggesting that the carbon does not dope in and distort the TiO$_2$ phase. However, it is found that the binding energy of Ti–O and C–O are weakened, which could infer that the CQDs are grafted onto the surface of TiO$_2$ via Ti–O–C bond. Besides, the reduced binding energy of Ti 2p (Fig. 2b) in 3 wt% CQDs/TiO$_2$ composite could suggest an electron-migration occurrence between TiO$_2$ and CQDs.

Since the XPS measurement merely analyzed the surface chemical state within a few nanometers in depth, ESR spectroscopy which enables an overall detection of the material was employed to further investigate the electron-migration phenomenon. Surprisingly, Ti$^{3+}$ defect (g = 1.98) [38] are detected in CQDs/TiO$_2$ samples while no such signal presents in pristine TiO$_2$ (Fig. 3a), and the Ti$^{3+}$ signals strengthen positively with the addition of CQDs. Since it is hard for Ti$^{4+}$ ion reduction happening during such mild and aerobic synthesized process [39], the existence of Ti$^{3+}$ defect could possibly originate from the different electron work function between CQDs and TiO$_2$. Due to special electron structure, the work function of CQDs might be lower than that of TiO$_2$, resulting in delocalized electron migration from CQDs to TiO$_2$, which makes the TiO$_2$ be negatively charged and form Ti$^{3+}$ defect, similar to the electron interaction between metal and semiconductor [40,41].

Viewing the result of UV–vis absorption spectra (Fig. 3b), CQDs/TiO$_2$ composites show an enhanced optical absorption in visible region compared with pristine TiO$_2$, and the absorption increases gradually with the CQDs addition, ascribed to the UCPL property [42]. Moreover, the absorption edges of modified TiO$_2$ also slightly red-shift, from ~400 nm to ~420 nm, suggesting the band gaps of composite photocatalysts narrow down after conjoining CQDs and the optical response correspondingly expand. Based on the aforementioned ESR results of CQDs/TiO$_2$ composites, the decreased band gaps of modified TiO$_2$ could result from the existence of Ti$^{3+}$ ion, which is capable of generating a defective energy level under conduction band [38].

### 3.2. Photocatalytic degradation of acetaldehyde

The photocatalytic ability for decomposing gaseous acetaldehyde via pristine TiO$_2$ and CQDs/TiO$_2$ composite samples were evaluated under the irradiation of household fluorescent lamp ($\lambda > 380$ nm, 20 mW cm$^{-2}$) and visible light ($\lambda > 400$ nm), respectively.

As shown in Fig. 4a, in the flowing gaseous acetaldehyde (500 ppm, 20 sccm), all CQDs/TiO$_2$ composite samples present an enhanced photocatalytic property over pristine TiO$_2$. After two-hour light irradiation, the pristine TiO$_2$ sample removes acetaldehyde by 46% and CQDs show no photocatalytic activity, while the highest degradation efficiency 99% can be achieved in 3 wt% CQDs/TiO$_2$ composite, of which the efficiency is two times as high as that of pristine TiO$_2$. It is worth mentioning is that since the gaseous acetaldehyde is continuously flowing into reactor chamber, it is reasonable for acetaldehyde not being thoroughly eliminated. As can be seen from the less acetaldehyde removal efficiency of 1 wt%
and 7 wt% CQDs/TiO₂ composites in Fig. 4a, further more or less addition of CQDs in composites could induce a relatively less improved photocatalytic performance, suggesting that a suitable amount of CQDs could effectively refine the TiO₂. Under the visible light irradiation (as shown in Fig. 4b), the 3 wt% CQDs/TiO₂ composite sample can eliminate 30% acetaldehyde, while the pristine TiO₂ shows an incapable photocatalytic performance (after light on, some previous absorbed acetaldehyde on TiO₂ surface desorbs due to the increased temperature by the significant heat effect under irradiation).

3.3. Adsorption of gaseous acetaldehyde

To investigate the reason for varied amounts of CQDs differently influencing the photocatalytic activity, the adsorbability for acetaldehyde via photocatalysts was then studied. The temperature programmed desorption (TPD) measurement result of pristine TiO₂ and 3 wt% CQDs/TiO₂ composite is reported in Fig. 5a, where the integral area of peak is corresponding with the amount of desorbed acetaldehyde and its further products during the thermal annealing process. The first peak at 110–120 °C is ascribed to the desorption of water and physically adsorbed acetaldehyde. The second peak, at around 200 °C could be involved with the products of acetaldehyde’s aldol condensation on the photocatalyst surface, for example, crotonaldehyde (CH₃CH=CHCHO), crotyl alcohol (CH₃CH=CHCH₂OH), and the third peak at 325–340 °C could be assigned to some olefins [43]. Viewing the spectra coverage, the total amount of desorbed substance of 3 wt% CQDs/TiO₂ composite is more than that of pristine TiO₂, so it can be inferred that the coupled CQDs could help with the adsorption of acetaldehyde, further assisting the photocatalytic process.

Additionally, the dynamic adsorption in the reactor chamber for flowing acetaldehyde gas upon all samples were tested and calculated (seeing Fig. 5b). The result of adsorption calculation indicates that the adsorption for acetaldehyde is positively correlated with the amounts of CQDs in the composites, which further supports the result of TPD measurement. And due to the contribution of CQDs, the improved adsorbability for acetaldehyde could be one of the reasons for enhanced photocatalytic property among all CQDs/TiO₂ composites. However, although more CQDs loaded on TiO₂ could help to promote the adsorption of acetaldehyde, superfluous acetaldehyde accumulation on photocatalyst surface might suppress the substance migration and the active sites of TiO₂ surface also would be covered by overloaded CQDs, both of which would result in a hindrance of photocatalytic process.

3.4. Photo-generated carrier recombination

The photoluminescence (PL) spectra of pristine TiO₂ and CQDs/TiO₂ composites are showed in Fig. 5c. Under 320 nm excitation at room temperature, all samples present a broad PL emission with a cascade of several peaks, located in 380–480 nm. Reasonably, it is the heterostructured nature consisted of anatase and rutile in the P25 that bring about the complexed PL emissions of which the photon energies are equal to band gaps of semiconductor. Taking all the emission spectrums in comparison, it is highlighted that the PL intensity decreases with raised CQDs concentration in CQDs/TiO₂. In pristine TiO₂, the photo-generated electrons which
are excited by photons transfer from exited state to ground state and recombine with holes, following by emission of fluorescence. While in CQDs/TiO₂ samples, the CQDs could serve as qualified electron reservoirs, and the photo-generated electrons on the conduction band of TiO₂ are inclined to migrate to CQDs. Therefore, under the influence of CQDs, the recombination of photo-generated electrons and holes could be effectively obstructed, which will benefit the photocatalytic process.

The photo-electrochemical experiment was carried out to investigate the photoinduced charge-transfer behavior. According to Fig. 5d, under visible light (λ > 400 nm) irradiation, all CQDs/TiO₂ samples show noticeable photocurrent responses while the pristine TiO₂ only has a very small photocurrent signal during several on-off cycles of irradiation. This phenomenon further proves that the modified TiO₂ could be activated under visible-light irradiation with the sensitization effect of CQDs, of which the result is rationally in accordance with the improved photodegradation behavior for acetaldehyde upon CQDs/TiO₂ (Fig. 4). Besides, the changing trend of photocurrent intensity is positively correlated with the mass of CQDs in composites. It suggests that CQDs play a significant role in the separation/transfer process of photo-generated charge carriers, resulting in a lowered recombination rate of photo-generated electron-hole pairs, which are in line with the PL result illustrated in Fig. 5c.

3.5. DMPO spin-trapping ESR spectra

Generally, the PCO process involves several reactive oxygen species, such as superoxide radical (O₂⁻), hydroxyl radicals (OH⁻) and hydrogen peroxide (H₂O₂), which play a vital role in the PCO process [44]. The ESR spin trapping technique was applied to investigate the radical species formed under xenon lamp irradiation of pristine TiO₂ and 3 wt% CQDs/TiO₂ composite, as shown in Fig. 6. It could be observed that after 5 min irradiation, pristine TiO₂ and CQDs/TiO₂ composite samples produce the typical radical intermediates. In the spectra, the four-line ESR signals with intensity ratios of 1: 1: 1: 1 and 1: 2: 2: 1 are respectively classified to the characteristic signals of DMPO-O₂⁻ and DMPO-OH adducts [45]. It is noticeable that the DMPO-O₂⁻ signals of the composites are much stronger than that of pristine TiO₂ in the same irradiative condition, and the 3 wt% CQDs/TiO₂ sample yields the most O₂⁻ species. The reasons for enhanced O₂⁻ production upon CQDs/TiO₂ composites could be explained as follows: (a) Due to the high electron affinity of dioxygen [46,47], the created Ti³⁺ defects with negative charge in the TiO₂ photocatalyst favor free O₂ adsorption. (b) Under the light irradiation, as the photo-generated electrons transfer to CQDs which also turns to be negatively charged, the suppressed electron-hole recombination induces more photo-generated electron to generate O₂⁻ radicals. However, excessive CQDs covered on TiO₂ might prohibit the photocatalytic activity and generate less charge carriers, matching with the consequence of above photodegradation test (Fig. 4a). Besides, judging from Fig. 6b, it indicates that introducing more CQDs to the composites would cause a negative effect on the formation of OH. Taken together, loading CQDs on TiO₂ surface benefits the O₂⁻ yield, which constitutes the dominated oxygen reactive species during the PCO process of CQDs/TiO₂ photocatalyst.
3.6. Discussion on photocatalytic mechanism

Based on the aforementioned experiment results, the photodegradation ability for acetaldehyde of photocatalyst gets enhanced after modified with CQDs, and the possible photocatalytic mechanism of CQDs/TiO₂ composite is illustrated in Fig. 7.

In the CQDs/TiO₂ composite, the CQDs are grafted onto TiO₂ via Ti-O-C bond, and some delocalized electron of CQDs migrate to TiO₂ due to the work function difference, resulting in the generation of Ti³⁺ defects in TiO₂ matrix and positively charged surface environment of CQDs. On one hand, through electron interaction, Ti³⁺ ions could favor the O₂ adsorption on photocatalyst surface; on the other hand, with graphite-like electron structure and functional groups (Fig. 1c), the CQDs could promote the composites to adsorb organic compounds, improving the contact with target gas and further benefitting the photo-degradation process, especially for the gaseous indoor pollutant in low concentration. But excessive amount of CQDs attached to TiO₂ might lead to suppress the photocatalytic performance owing to reduced active sites on photocatalyst surface, and impeded migration of excessive adsorbed acetaldehyde.

After coupling with CQDs, the visible-light harvesting has been significantly improved in the modified TiO₂ photocatalyst. Understandably, the formation of Ti³⁺ donor energy level could narrow the band gap as Fig. 7 shown. Furthermore, through CQDs, some visible light could be harvested and upconverted to higher-energy photon for PCO excitation. In addition, the recombination of photo-generated electrons and holes in the CQDs/TiO₂ composite also get limited which is confirmed by the results of PL spectra and photocurrent response (Fig. 5c and 5d). Serving as remarkable electron reservoirs, the CQDs could harvest and stock photo-generated electron from conduction band of TiO₂, to hinder the recombination of electron-hole pairs and further facilitate the photocatalytic activity. Under light irradiation, the trapped photo-generated electrons on CQDs could further reduce the absorbed O₂ to reactive ‘O₂⁻, of which the production could depend on the photo-generated carrier separation efficiency and the amounts of photo-generated electron trapped by CQDs. Thus the enhanced electron-hole separation efficiency directly boosts the ‘O₂⁻ formation as substantiated in the DMPO spin-trapping ESR measurement (Fig. 6a).

4. Conclusion

In summary, the CQDs/TiO₂ heterostructured photocatalyst has been constructed and firstly applied to photodegrade flowing gaseous acetaldehyde under visible-light irradiation. Compared with the degradation efficiency 46% obtained by pristine TiO₂, the highest photodegradation efficiency 99% can be acquired based on the optimal photocatalytic performance of 3 wt% CQDs/TiO₂ under fluorescent lamp irradiation. And under visible-light irradiation, the 3 wt% CQDs/TiO₂ remained 30% removal efficiency while pristine TiO₂ showed no photocatalytic ability. The optimized photocatalytic performance of the composite could be ascribed to the conjoined CQDs for three aspects: (a) facilitating visible-light harvest by the formation of Ti³⁺ donor energy level and up-converted photoluminescence property of CQDs; (b) improving adsorption for...
organic compounds due to the graphite-like electron structure and intrinsic functional groups of CQDs; (c) as an electron reservoir, inhibiting the recombination of photo-generated carriers and promoting the reduction of $\mathrm{O}_2$. This work not only provides a heterostructured CQDs/TiO$_2$ composite material to efficiently photodegrade the flowing gaseous acetaldehyde, but also reveals some new functions of CQDs in the semiconductor-based photocatalytic mechanism. Since the CQDs/TiO$_2$ composite is capable of visible-light response with an enhanced photocatalytic ability for acetaldehyde removal, this promising composite photocatalyst could be expected as a qualified candidate for further indoor-air-purification applications.

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Conflict of interest

The authors declare no competing financial interest.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.01.104.

References


